

UOP

petrochemical

Process Technology and Equipment

UOP Butene-1 Production Process

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Technology selection for the production of high-purity butene-1 depends on the producer's need, or lack of need, for butadiene. Butadiene constitutes 40-50% of the C_4 cut of a steam cracker and can either be recovered via extraction or be converted to mono-olefins (butene-1 and butene-2) by selective hydrogenation. Both cases will be discussed here. A typical C_4 cut composition is shown below.

Steam Cracker C_4 Cut

	wt.-%
Acetylenes	1
Butadiene	45
Isobutene	26
Butene-1	14
Butene-2	9
Butanes	5

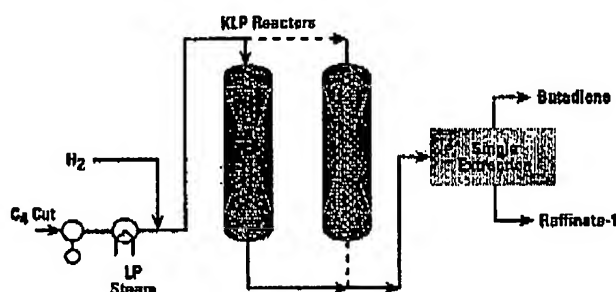
COPRODUCTION OF BUTADIENE—
KLP™ PROCESS/EXTRACTION

If butadiene (BD) is a desired product, it can be extracted using commercially available technology. Prior to the extraction unit, the KLP process is used to convert essentially 100% of acetylenes to mono-olefins and BD. A simplified KLP process flow diagram (PFD) is shown in Figure 1.

The highly selective nature of the KLP process results in no hydrogenation of BD. The process requires two reactors, one of which is being regenerated at any given time. With acetylene no longer present, the extraction of simpler than conventional two-stage extraction units. The extracted BD is very high purity, with total acetylene levels typically less than 5 ppm.

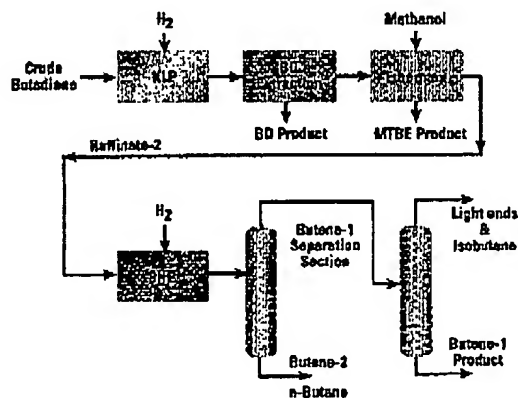
The raffinate from the extraction unit, termed raffinate-1, is charged to an Ethermax™ unit in which isobutylene is reacted with methanol. Unreacted C_4 , termed

Figure 1
Coproduct of Butadiene and Butene-1
KLP with Extraction



raffinate-2, is then charged to a Hüls SHP process unit and subsequently to fractionation for the separation of butene-1. These processes are described below (Figure 2).

Figure 2
UOP C_4 Processing



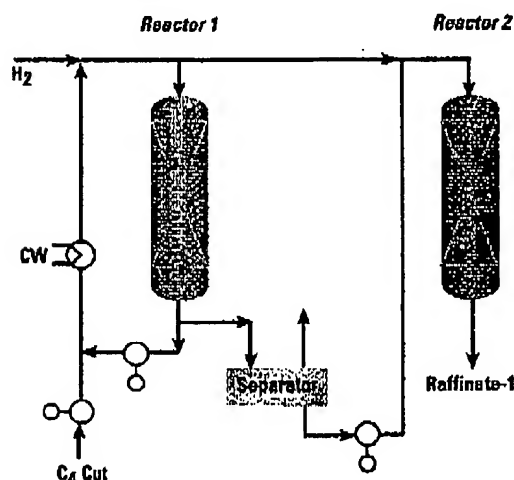
The KLP process operates at low temperatures, with a slight exotherm and moderate pressure, which is adequate to keep hydrogen in solution.

The SHP process also operates at mild temperatures and moderate pressure. The process requires a slight excess of hydrogen. The product typically contains less than 10 wt ppm diolefins.

HYDROGENATION OF BUTADIENE—HÜLS SHP-CB™ PROCESS

If the producer has no need to extract butadiene, the Hüls SHP-CB process can be used to selectively hydrogenate the BD in the C_4 cut by converting it to butene-1 and butene-2. Acetylenes and dienes are likewise hydrogenated. (A simplified flow scheme is shown in Figure 3.)

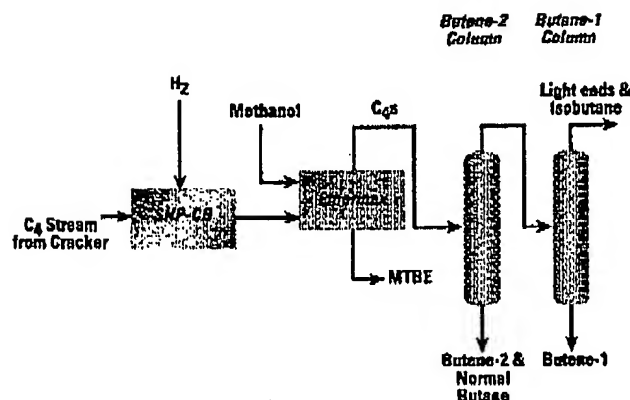
Figure 3
Hüls SHP-CB Process



If the process is optimized to produce butene-1, about 60% of the BD is converted to butene-1. The SHP-CB process, configured for this case, would be a three-stage process for maximum butene-1 selectivity. The first stage reduces the BD level to ~3.0 wt-%. The second stage further converts BD so that the outlet concentration is nominally 1.0%. The third stage reduces the BD to approximately 10 wt ppm.

The process is operated in the liquid phase at mild temperatures and moderate pressures. The product from the SHP typically contains 10 wt ppm diolefins.

Figure 4
Butene-1 Production



The catalyst used in the system is extremely selective to diolefin saturation, such that a net gain in mono-olefins, equal to the conversion of diolefins, is achieved. The system has a product recycle loop that allows the level of diolefins and the temperature of the feed to be controlled at a desired level. This is important to maximize butene-1 selectivity and to minimize catalyst coking.

The SHP-CB process requires little or no recycle hydrogen to operate. This makes the process more attractive, especially when compared to a first-stage hydrotreater.

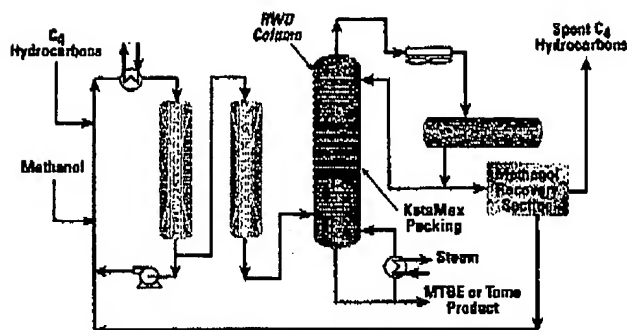
Product from the SHP-CB process is charged to the Ethermax unit and subsequently to fractionation. These processes are conceptually the same as for the BD extraction option (Figure 4).

ETHERMAX UNIT

In an Ethermax unit the isobutylene is removed by converting it to MTBE by reaction with methanol (MeOH) as shown in Figure 5. High conversion of isobutylene is necessary for high-purity butene-1 production because isobutylene and butene-1 boil at -7°C and -6°C , respectively, so fractionation would be extremely difficult.

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Figure 5
Ethermax Process



Although there are other commercially available etherification processes, the Ethermax process provides the most economical alternative to meet butene-1 specifications. Also, isobutylene conversion in the Ethermax unit is at least 99.9%, which removes enough isobutylene to meet the typical spec of <0.1 wt-% in the butene-1 product.

The catalyst used in the Ethermax unit is a sulfonic acid ion-exchange resin. The resin is available from Dow Chemical, Bayer, or Rohm & Haas. The high conversion level is obtained by overcoming the fixed-bed reaction equilibrium constraint. The reaction:



is equilibrium limited. By using the RWD technology, equilibrium is overcome because the MTBE is separated out by fractionation from the isobutylene and methanol, allowing the reaction to continue to nearly 100% conversion. The RWD technology uses Koch Engineering's KataMax™ packing. This structured packing not only contains resin to catalyze the reaction, but also has very good mass transfer properties for separation. This is a key advantage to UOP's technology.

HÜLS BUTENE-1 RECOVERY PROCESS

Once the isobutylene has been removed, the C₄ raffinate is sent to the Hüls butene-1 recovery process. The separation of the different C₄ components by fractionation is fairly difficult. The first column removes normal butane and butene-2 in the bottom and sends the butene-1 and light ends overhead. The butene-1 is then taken as the bottoms product in the next column. These columns are rather large: ~200 trays. Traditionally, in a large plant each column had to be built with two shells because of the height. With UOP's MD™ trays, the columns can fit into one shell, providing a significant cost savings. UOP's experience designing and operating these columns is another big advantage.

EXPERIENCE

As shown below, UOP has extensive commercial experience with the technologies involved in the process.

Hüls SHP, SHP-CB - 20 units in operation by 2002

Ethermax process - 6 units on stream, a total of 16 units licensed

KLP process - 8 units in operation by 2001

UOP has two integrated butene-1 production complexes on stream. Several others are under consideration.

FOR MORE INFORMATION

For more information, contact your local UOP representative or contact our Des Plaines sales office:

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